On Possible Coexistence of Superconductivity and Charge Density Wave in Hole-doped C_{60}

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Abstract

Superconductivity in C_{60} materials is modeled in terms of an intramolecular, nonretarded attraction. It was shown previously that, at intermediate coupling, the model possesees a state in which s-wave superconductivity coexists with a charge density wave, the latter stabilized by intersite repulsion. The CDW causes T_c to decrease near half filling. We argue that hole-doped C_{60}, for which T_c peaks away from half filling, is a possible candidate for this state. But the electron-doped C_{60} and A_3C_{60} are conventional superconductors, stabilized against a CDW by metallic screening, which is treated in a parameter-free fashion.

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About a decade ago, superconductivity with surprisingly high T_c's $(30-40K)$ was observed in A_3C_{60}, where A is an alkali atom [1, 2]. Recently much higher T_cs $(52K-117K)$ have been seen in hole-doped C_{60} [3, 4]. Within the Bardeen-Cooper-Schrieffer (BCS) picture, origin of such high T_c's has been attributed to special properties C_{60}, such as, high density of states (DOS) and large phonon frequency. However, variation of T_c with the density n does not follow the DOS. Also, in the electron-doped C_{60} and A_3C_{60} the maximum of T_c occurs near half filling. But in the hole-doped material, T_c peaks at a density of $n = 3 - 3.5$ holes/molecule, and decreases rapidly toward half filling (5 holes/molecule) [3]. Such a behavior has been predicted previously on theoretical grounds[5, 6]. The sharp decline in T_c is caused by the appearance of a charge density wave (CDW) near half filling which, due to the frustration effects of the lattice, can coexist with superconductivity. Here we examine the conditions for the existence of such a state in C_{60}.

The possibility of a CDW instability in C_{60} was recognized early by Zhang, Ogata and Rice[8]. As discussed below, it becomes more likely as T_c increses. The key issue is the effect of Coulomb repulsion which opposes superconductivity, but favors the CDW. We will focus mostly on the normal state, and consider realistic potentials. We find that if there is no metallic screening, the

energy gained by the CDW increases monotonically with increasing interaction strength. However, in the presence of metallic screening, the gain has a *maximum*. It is too small to stabilize the CDW state in the lower T_c materials such as A_3C_{60}. But for the hole-doped case, the CDW state can not be ruled out. We discuss some normal-state anomalies of this state.

Crystalline C_{60} has a face-centered-cubic (FCC) structure, and is a semiconductor. The conduction band is formed from the 3-fold degenerate t_{1u} molecular orbitals, and the valence band from the 5-fold degenerate h_{1u} orbitals. In A_3C_{60}, each alkali atom donates one electron to the conduction band making it half-filled. Large molecular size leads to a large lattice spacing ($a \sim 10\mathring{A}$), and consequently very narrow bands [7] of width $W \sim 0.5eV$, which can thus be adequately described by a tight-binding model with nearest-neighbor hopping. This implies that geometric effects such as *frustration* and *nesting* are important.

Our theory is based on two key assumptions. (1) Low energy physics of the doped system can be described by an effective Hamiltonian defined entirely within the relevant band, i.e., the h_{1u} band for hole-doped C_{60}, and the t_{1u} band for electron-doped C_{60} and A_3C_{60}. The effect of integrating out other bands and phonon degrees of freedom is to renormalize the interactions. (2) The attractive interaction responsible for superconductivity is intramolecular in origin and effectively *nonretarded*, i.e, the characteristic frequency ω_0 is comparable to the Fermi energy. Indeed, intramolecular phonons that are thought to be responsible [3] have rather high frequencies: $\hbar\omega_0 \sim 0.15eV - 0.2eV$, easily comparable with the Fermi energy.

The model always has a solution in which the normal state is conventional, and superconductivity is BCS like. In the BCS theory T_c is given by

$$kT_c \approx 1.3\hbar\omega_0 e^{-1/\lambda}, \tag{1}$$

where $\lambda \approx U\rho(\epsilon_F)$ is the dimensionless coupling constant, $\rho(\epsilon_F)$ is the density of states (DOS) at the Fermi level, U is the attractive interaction. The observed high T_c's are usually[3] attributed to: (1) a relatively high DOS due to the narrow bandwidth ($\rho \propto W^{-1}$) and orbital degeneracy, and (2) a large prefactor due to high phonon frequency. Furthermore, in A_3C_{60}, T_c increases with increasing size of the alkali atoms. This is because as the lattice expands, W decreases. Similarly, the five-fold degeneracy of the h_{1u} level should lead to higher DOS [7], which will account for the higher T_c in the hole-doped material.

However, not everything fits. According to the simple BCS formula, the n-dependence of T_c should track that of the DOS (through the n-dependence of the Fermi energy). This is actually not the case. For the FCC lattice the DOS has sharp features. The measured T_c is smoother, its maximum is far removed from that of the DOS, both for the electron doped or hole doped materials[3].

We point out that the problem is partly due to the assumption that the attractive interaction is retarded, i.e., confined within $\hbar\omega_0 << \epsilon_F$ of the Fermi

surface. Then one can approximate the DOS by $\rho(\epsilon_F)$, and use $\hbar\omega_0$ as a cut-off in the energy integral which accounts for the prefactor. This procedure is not valid when $\hbar\omega_0$ is comparable to ϵ_F. In fact, as shown previously[6], in the nonretarded case T_c varies much more smoothly with n. The reason is that for general values of $\hbar\omega_0$, a more accurate approximation is given by

$$kT_c \approx 1.3\hbar(w_1 w_2)^{1/2} e^{-1/\rho_0 U},$$

where $\hbar w_1 = min(\epsilon_F, \hbar\omega_0)$, $\hbar w_2 = min(W - \epsilon_F, \hbar\omega_0)$, and ϵ_F is measured from the bottom of the band. Here ρ_0 is the weighted average of the DOS $\rho(\epsilon)$ over the allowed region with a slowly varying weight factor $\epsilon^{-1}\tanh(\epsilon/2kT_c)$ (normalized to unity). For small $\hbar\omega_0$ we recover the usual BCS formula, whereas for large $\hbar\omega_0$, the variation of T_c with n is smoothed out considerably. In this case, a better estimate is $\rho_0 \approx 1/W$.

A more important issue is the possibility of a CDW instability which can not be ignored when $\hbar\omega_0$ is comparable to ϵ_F. We consider a one-band model, characterized by a single-particle energy $\epsilon_{\mathbf{k}}$, an on-site attraction U, and an intersite repulsive interaction $V(\mathbf{r})$. The relevant dimensionless energy scales are $U\rho$ and $V\rho$. The effect of orbital degeneracy can be approximately taken into account by changing ρ, or, equivalently, by changing U/W and V/W. The possibility of a CDW was studied in reference [8] using this model, but without the V term. However, as shown previously, inclusion of even a nearest neighbor V leads to nontrivial consequences [5, 6]. We now generalize to $V(\mathbf{r})$ of arbitrary range.

In the simplest mean-field approximation, and in the absence of superconductivity, a CDW with a wavevector $\mathbf{Q}$ would appear for

$$(U + 2V_{\mathbf{Q}})\chi(\mathbf{Q}) > \mathbf{1}, \tag{2}$$

where $\chi(\mathbf{Q})$ is the charge susceptibility for the noninteracting system, and $V_{\mathbf{Q}} = -\sum_{\mathbf{r}\neq 0} e^{i\mathbf{Q}.\mathbf{r}} V(\mathbf{r})$. The minus sign is included in order to make $V_{\mathbf{Q}}$ positive. For a bipartite (e.g., simple cubic, BCC etc) lattice, there is a $\mathbf{Q}$ for which

$$\epsilon_{\mathbf{k}+\mathbf{Q}} = -\epsilon_{\mathbf{k}} \tag{3}$$

for all $\mathbf{k}$. Then the Fermi surface is perfectly nested at half filling, leading to a logarithmically divergent χ at $T = 0$ and a CDW instability for any $(U+2V_{\mathbf{Q}}) > 0$. For the nonbipartite FCC lattice, $\chi(\mathbf{Q})$ is finite *even at half filling* as there is no nesting, i.e., no $\mathbf{Q}$ for which Eq.(3) holds. A conventional metallic state is then stable for $(U + 2V_{\mathbf{Q}}) < 1/\chi(\mathbf{Q}) \approx 0.375W$. Above this, a CDW state appears with $\mathbf{Q} = (0, 0, 2\pi/a)$, which corresponds to a CDW with a density $n(\mathbf{r}) = n + n_1 e^{i\mathbf{Q}.\mathbf{r}}$, i.e., on successive planes perpendicular to the z axis, the density alternates between $n + n_1$ and $n - n_1$.

From (2), it appears that a CDW can exist even $V = 0$. However, such a state is unstable against s-wave superconductivity, since the pair susceptibility is logarithmically divergent. The inclusion of $V(\mathbf{r})$ changes this picture,

due to two reasons. First, the V term favors the CDW energetically. At the mean-field level, the excess potential energy per site in the CDW state equals $-(U+2V_Q)n_1^2/4$. Physically, the CDW forms an "ionic crystal" with $V_{\mathbf{Q}}$ proportional to the appropriately generalized Madelung energy[9]. However, compared with a bipartite (e.g., BCC) lattice, charge ordering on an FCC lattice is *frustrated*, leading to a somewhat lower energy gain. Nonetheless, we have verified numerically that $V_Q > 0$, for the screened Coulomb potentials (Fig 1) which are the potentials of interest. Second, $V(\mathbf{r})$ always opposes superconductivity by keeping particles apart, stabilizing the CDW state at larger $V_{\mathbf{Q}}$.

The CDW splits the noninteracting band into two bands of energy

$$E_{\pm}(\mathbf{k}) = \epsilon_1(\mathbf{k}) \pm [\epsilon_2^2(\mathbf{k}) + \Delta_C^2]^{\frac{1}{2}}, \tag{4}$$

where $\epsilon_1(\mathbf{k}) = \frac{1}{2}(\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}+\mathbf{Q}})$ and $\epsilon_2(\mathbf{k}) = \frac{1}{2}(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{Q}})$. At the same $\mathbf{k}$, the bands are separated by a gap $\Delta_C = n_1(U + 2V_{\mathbf{Q}})/2$. For a bipartite lattice the geometrical property, Eq. (3), ensures that $\epsilon_1(\mathbf{k}) = 0$, leading to insulating behavior. However, Eq.(3) does not hold for the FCC lattice. Then for small enough Δ_C, the maximum of the lower band lies above the minimum of the upper band which, in general, is at a different $\mathbf{k}$ point. This leads to a semimetal with a partially gapped Fermi surface. The is a direct consequence of geometric properties frustration and (lack of) nesting. Eventually, there is a transition to a an insulating state for $(U + 2V_{\mathbf{Q}}) > 0.562W$.

Furthermore, residual attractive interaction within the semimetal leads to superconductivity. For a nearest-neighbor V, the CDW has been shown to coexist with superconductivity over a substantial region in the parameter space [5]. The presence of the CDW lowers T_c, and yields [6] a $T_c(n)$ which is very different from that in the conventional state (no CDW). In either case, T_c does not track the DOS. In the conventional state, it peaks near half filling and gradually decreases to zero at the band edges. This is similar to the behavior observed in electron doped C_{60} and A_3C_{60}.

By contrast, in the CDW-superconductor T_c has a *minimum* near half filling where the CDW instability is strongest. Away from half filling, T_c increases as the CDW weakens. Eventually, there is a transition to the conventional state. Consequently T_c reaches a maximum near the transition point and then decreases following the behavior in the conventional state. This is very similar to the behavior observed in the hole doped C_{60}. So far only one maximum has been seen because experiments have been limited to only one side of half filling. The theory predicts two, one on each side. These results should be qualitatively correct for the more realistic screened Coulomb potential, although one expects a more rapid decline of T_c toward the band edges since screening length increases with distance between particles.

Are the observed T_c's consistent with the theory? Consider the conventional state at half filling which exists for $(U + 2V_{\mathbf{Q}})/W < 0.375$. To estimate U/W from the measured T_c, we use formula (1), conveniently rewritten as

$1/\lambda = -ln(kT_c/1.3\hbar\omega_0)$, to compute λ, which is treated as a phenomenological coupling constant. At half filling, we can take ω_0 to be the (intramolecular) phonon frequency, which is same for all materials. Noting that λ varies slowly with ω_0, we set $\hbar\omega_0 = 1500K$, which is reasonable. For the electron doped C_{60} ($T_c = 11K$) this gives $\lambda = 0.146$. However, for Rb_3C_{60} ($T_c = 33K$), $\lambda = 0.245$. Next step is to relate λ with the theoretical parameter U/W. As discussed before, in the absence of $V(\mathbf{r})$, and for large $\hbar\omega_0$, $\lambda \approx U/W$. However, when $V(\mathbf{r})$ is included, λ will be reduced so that $U/W > \lambda$. This means that electron-doped C_{60} and A_3C_{60} can be conventional metals, but for the larger alkali (Rb etc) materials $V_{\mathbf{Q}}/W$ has to be rather small.

For the hole-doped C_{60}, the maximum T_c of $52K$ yields a larger value of λ (≈ 0.28) which could be sufficient for the CDW state. However, the maximum is away from half filling which in our theory is due to the transition to the CDW-superconducting state. In order to be consistent, we have to use the T_c of the corresponding conventional state at half filling. This is about 30 to 50 percent higher, which gives $U/W > \lambda \sim 0.32 - 0.34$. For any reasonable values of $V_{\mathbf{Q}}$ these materials should be CDW metals near half filling. Any expansion of lattice will increase U/W, making the CDW even more likely [4].

The intriguing question is, why is A_3C_{60} not a CDW metal, as suggested previously[5]? For example, for Rb_3C_{60} to be conventional, $V_{\mathbf{Q}}/W$ has to be ~ 0.05 or less, almost two orders of magnitude smaller than the bare Coulomb energy scale $e^2/a \approx 2.6W$. Now, there are two sources of screening. (1) Screening by other molecular bands which can be approximated by a static dielectric constant ϵ. One expects ϵ to be somewhat larger than that in ordinary semiconductors because of small (molecular) band gaps. (2) Since the transition is from one metallic state to another, we must include *metallic* screening which leads to exponentially short-range potential and much smaller $V_{\mathbf{Q}}$. To see this, we consider the screened Coulomb potential

$$V(\mathbf{r}) = \frac{e^2}{\epsilon r} e^{-r/\xi}, \tag{5}$$

where ξ is the Thomas-Fermi screening length.

Let us define the dimensionless quantity α by writing $V_{\mathbf{Q}} = v_0\alpha(\xi/a)$, where $v_0 = e^2/\epsilon a$ sets the energy scale for the long-range part. Then $\alpha(x)$ is generalized Madelung constant [9], defined for screened-Coulomb potential. As shown in Fig. (1) α, which measures the energy gained by the CDW, increases with the range of interaction ξ/a. In the absence of metallic screening, $\xi = \infty$, and $\alpha \approx 1.6$. With decreasing ξ, α decreases rapidly below $\xi \sim a$, which is essentially the metallic region. Fig. 1 also shows that α is always smaller for the FCC lattice than the bipartite BCC lattice. This is due to frustration which is another — albeit smaller – source of reduction of $V_{\mathbf{Q}}$.

It is possible to have a CDW state in every case by choosing the parameters v_0 (i.e., ϵ) and ξ appropriately. However, a much better *parameter-free* understanding of screening can be obtained as follows. First, note that ξ itself

depends on v_0. The Thomas-Fermi expression for ξ [10], written in the lattice language, reads:

$$\xi/a = [(4\pi\gamma v_0)\frac{dn}{d\mu}]^{-1/2}, \tag{6}$$

where μ is the chemical potential, and the geometrical parameter $\gamma = \sqrt{2}$ for the FCC lattice. At low T, $dn/d\mu \approx \rho(\epsilon_F) \sim 2/W$. Let us define an effective bandwidth by $2/W_{eff} = dn/d\mu$. Since α depends only on ξ/a, we see that the dimensionless quantity $V_{\mathbf{Q}}/W_{eff}$ is a universal function of the dimensionless coupling constant v_0/W_{eff} only. This is plotted in Fig. 2. Notice that $V_{\mathbf{Q}}/W_{eff} \sim V_{\mathbf{Q}}/W$, the quantity of interest. Naively one would expect $V_{\mathbf{Q}}$ to keep increasing as v_0 increases. On the contrary, $V_{\mathbf{Q}}/W_{eff}$ has a broad maximum. This is because an increased v_0 (i.e., a larger charge) makes the screening length ξ shorter (Eq. 6) which decreases α. The maximum occurs at $\rho v_0 \approx 0.15$ and has a value of about 0.042. This is a pure number, which depends only on the lattice type, but not any parameters. Hence, we have the remarkable result that irrespective of how large or small v_0 (i.e., ϵ) is, $2V_{\mathbf{Q}}/W_{eff} < 0.084$. The smallness of this number, combined with the above estimates of U/W, explains why A_3C_{60} is conventional. We stress that this drastic reduction of $V_{\mathbf{Q}}$ would not occur if the CDW state were an insulator since there is no metallic screening at the transition.

Since $V_{\mathbf{Q}}/W_{eff}$ varies slowly (fig. 2), its maximum value also provides an estimate for its magnitude. For example, $2V_Q/W_{eff} > 0.06$ in the entire range of $0.05 < v_0/W_{eff} < 0.4$ ($52 > \epsilon > 6.5$). This is sufficient for the hole-doped C_{60} to be a CDW semimetal. This analysis is of course approximate. One way to see if the state is experimentally realized is to look for normal state anomalies.

The semimetal is described in terms of two bands separated by a direct gap $\Delta_C(T)$, as well as a Fermi surface. The gap vanishes at T_{CDW}, above which the normal state is conventional. Below T_{CDW}, the band parameters become temperature dependent through $\Delta_C(T)$, leading to distinct features. Thus, the carrier density becreases with increasing Δ_C, leading to peak or a shoulder in the resistivity as a function of T. Other quantities, such as the specific heat, also show similar behavior. To see this, consider the approximate low T expression for energy

$$E(T) = E_0(\Delta_C) + \frac{\pi^2}{6}(kT)^2\rho(\epsilon_F), \tag{7}$$

where $E_0(\Delta_C)$ is the ground-state energy and ϵ_F is the corresponding Fermi energy for a given $\Delta_C(T)$. For $T > T_{CDW}$, $\Delta_C = 0$, and E_0 and ρ are independent of T, leading to linear heat capacity and T-independent magnetic susceptibility. Below T_{CDW}, E_0 and $\rho(\epsilon_F)$ become temperature dependent through $\Delta_C(T)$. We have solved the mean-field equations numerically at finite T. Fig. 3 shows typical behavior of specific heat as a function of T/T_{CDW}, which is linear in T above $T > T_{CDW}$, and again becomes linear at low T, as $\Delta_C(T)$ saturates, but with a smaller slope, corresponding to reduced value of $\rho(\epsilon_F)$. The sharp feature

below T_{CDW} is due to the rapid decline in $\rho(\epsilon_F)$ as function of temperature, also shown in Fig. 3. These features should be experimentally observable in the region where $T_{CDW} > T_c$, i.e., close to half filling.

In conclusion, we have shown that despite relatively high T_c's, frustration and metallic screening suppresses a CDW instability in A_3C_{60}. But for hole-doped C_{60}, a mixed state can not be ruled out. If the anomalies discussed above are not observed, then the CDW is absent. This is possible, given the simplicity of the model and approximate nature of the analysis. Even then the instability can not be be very far away, and can occur as T_c is increased further by lattice expansion. The author thanks C. Jayaprakash and T. L. Ho for discussions.

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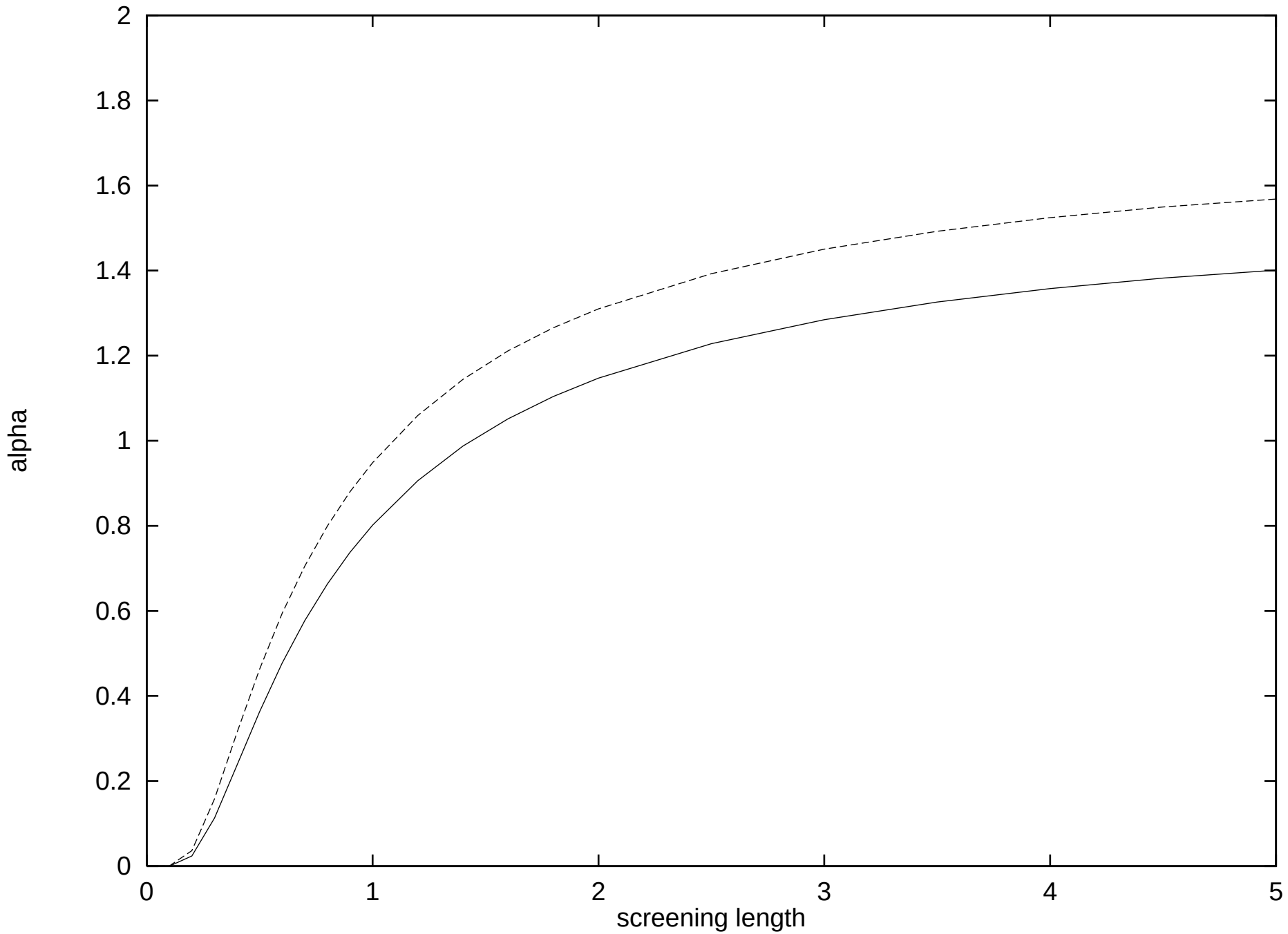
[10] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, p341. Note, in our case n measures number of particles per site.

FIGURE CAPTIONS

Fig.1: The generalized Madelung constant $\alpha = V_{\mathbf{Q}}/v_0 = \sum_{\mathbf{r}\neq 0} \frac{e^{i\mathbf{Q}.\mathbf{r}-\mathbf{r}/\xi}}{(r/a)}$ plotted against dimensionless screening length ξ/a, where a is the nearest neighbor distance. Note that α depends only on ξ/a and the lattice type. The solid line is for the FCC lattice and the dashed line for the bipartite BCC lattice, showing that energy gain from the CDW is less for the FCC lattice due to frustration. In usual metals, $\xi/a < 1$.

Fig.2: The dimensionless quantity $V_{\mathbf{Q}}/W_{eff}$ is plotted (solid line) against v_0/W_{eff} where $W_{eff} = 2/\frac{dn}{d\mu} \sim W$. Also shown (dashed line) is $10\xi/a$ which, like α, is slowly varying except for very small v_0.

Fig.3: Scaled specific heat (solid line) and density of states at the Fermi level (dashed line) are plotted vs T/T_{CDW} for the CDW-metal at half filling. The parameter values are $U+2V_{\mathbf{q}} = 6.71t$, $T_c = 0.768t$, The prominent feature below T_{CDW} is due to the CDW and reflects the rapid rise in the DOS.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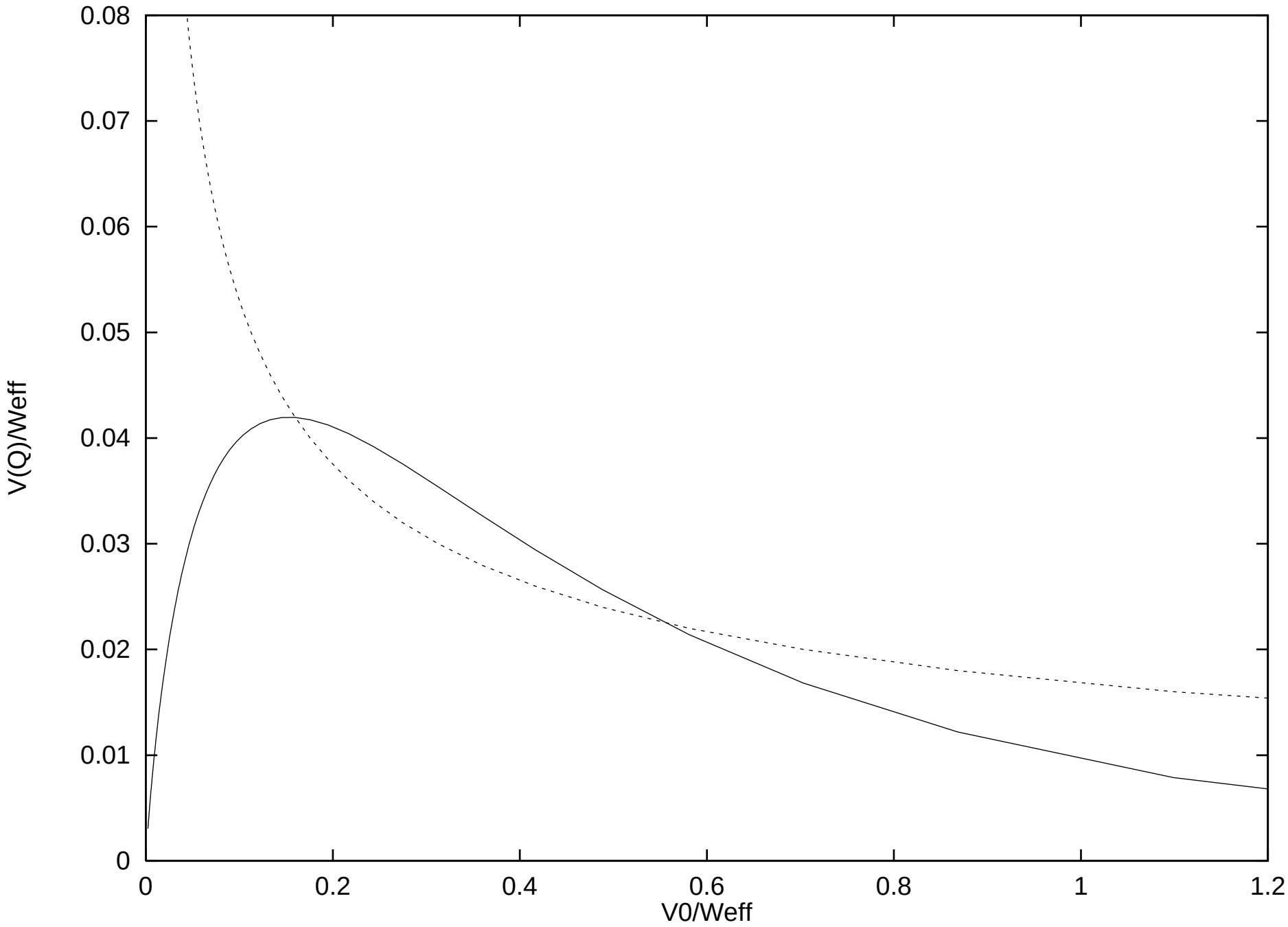
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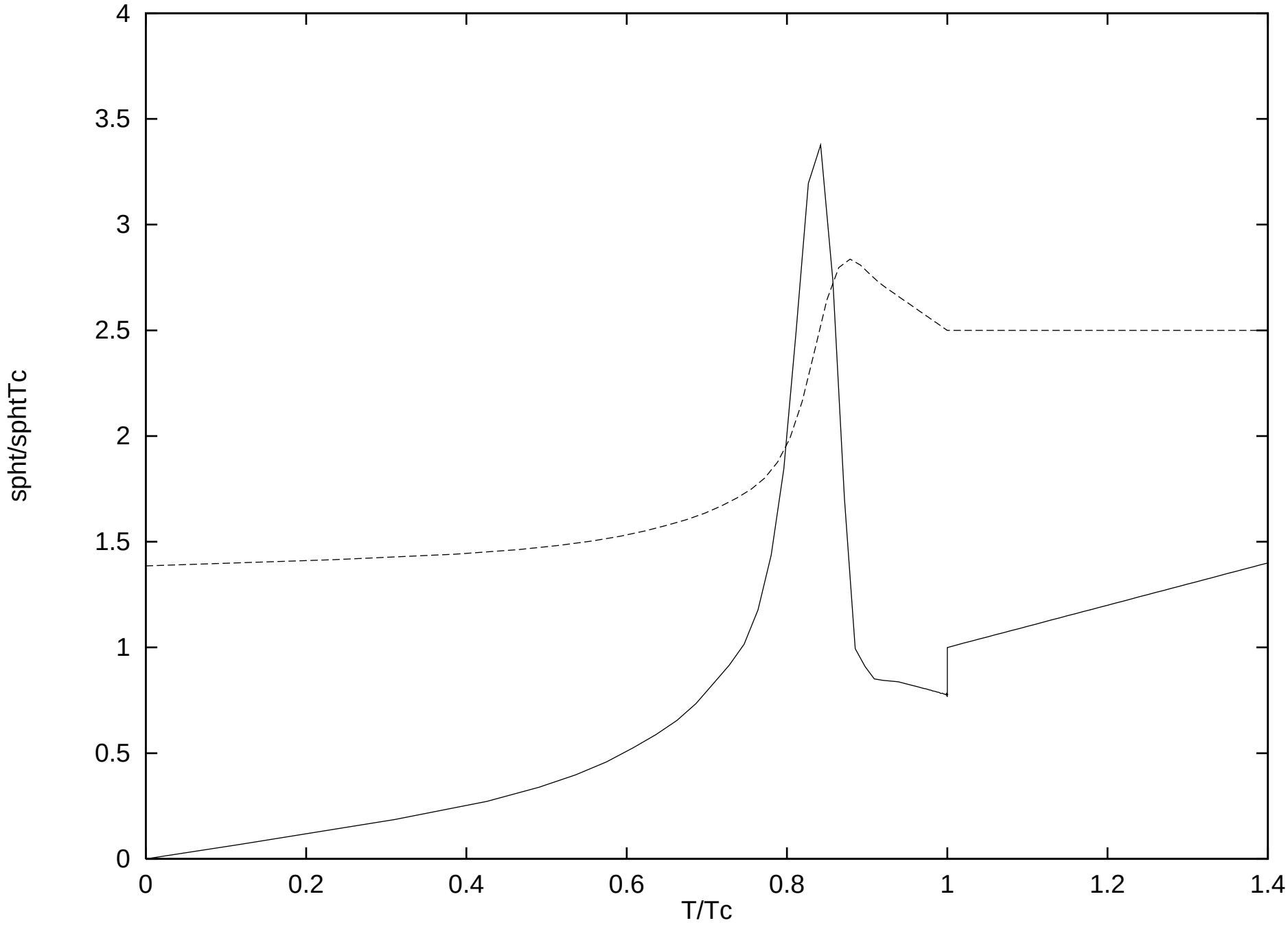
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